Ion Concentration at the Membrane Surface Obtained from the Membrane Potential and Transition of Ion Cluster Structure in Perfluorocarboxylate Ion Exchange Membrane System

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The fast step and the subsequent slow step have been observed in the time course of the membrane potential in response to pH jump in the perfluoro carboxylate ion-exchange membrane-aqueous NaCl system. Using the Donnan potential obtained by separation of the two steps, the ion concentration at the membrane surface has been estimated. A change in the ion-cluster structure in the membrane has caused the plot of the surface concentration vs. pH in the external solution to break.

In charged membrane-aqueous electrolyte system, the electrical potential difference (Donnan potential) is generated across the membrane/solution interface originating in the surface charge due to ionized groups of the membrane surface[1,2]. The evaluation of the Donnan potential for those membranes had been difficult in the nonequilibrium state so far. It has been demonstrated in this study that the total membrane potential observed in a reverse permeation system can be divided in its constituents, the Donnan potential and the diffusion potential within the membrane on the basis of the transient membrane potential measurement. The perfluorinated polymer membrane is microheterogeneous in structure, i.e., the hydrophobic region formed by the fluorocarbon chain of polymer backbone and the hydrophilic region formed by clustering the ionic groups of the polymer and counter ions and water molecules called ion-cluster are dispersed like a reverse micellar system[3-5]. The ion cluster structure varies depending on the types of the counter ions.[4] In the present system in which the membrane separates the alkaline and acidic solutions of NaCl, the effect of the change in the cluster structure on the Donnan potential obtained from the transient membrane potential and that on the counter-ion concentration at the membrane surface estimated from the Donnan potential have been significantly shown in these pH dependencies as breaks.

The perfluoro carboxylate polymer membrane (Flemion 230 kindly supplied by Asahi Glass, with ion exchange capacity of 1.4 mmol univalent ion/g dry) was used as a cation exchange membrane. The polymer is prepared by copolymerization of tetrafluoroethylene with perfluoro vinyl ethers having COOH groups. The internal solution, solution II, contained 0.1 mol dm^{-3} NaOH and 0.1 mol dm^{-3} NaCl and the external solution, solution I, contained 0.2 mol dm^{-3} NaCl and HCl of various concentrations. The time course of the membrane potential in response to a pH jump in the solution I was followed by means of a pair of Ag/AgCl reference electrodes with liquid junction (Model K-801, Radiometer) connected to an electrometer (Model 614, Keithley). An abrupt change in pH of solution was achieved by injecting HCl solution from the tip of an auto-piston burette (Model APB-410, Kyoto Electronics) while keeping the concentration of sodium ions constant and stirring the external solution as well as the internal solution by a magnetic stirrer. All the measurements were carried out at 25.0 °C. In these membrane systems, Na$^+$ ions can be transported from the alkaline side against its own concentration difference. This reverse permeation has been confirmed by the atomic absorption spectroscopy, which will be described in a separate paper.

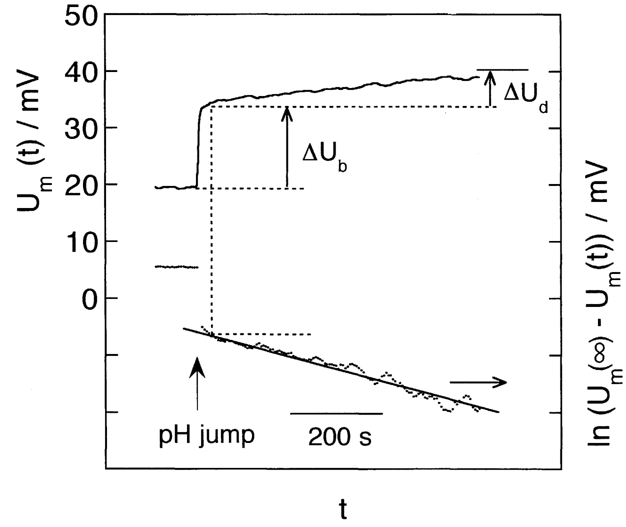

Figure. 1. A typical time dependence of the membrane potential in a transition between two steady potentials. Concentration jump of HCl in the external solution was from 2 x 10^{-2} mol dm^{-3} to 6 x 10^{-2} mol dm^{-3}. The internal solution contained 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH.

In Figure 1, it is demonstrated that the time course of the membrane potential ($U_m = \phi^{II} - \phi^{I}$; where ϕ^{I} and ϕ^{II} refer to the electrical potential in solutions I and II, respectively.) in response to a change in the pH of the external solution consists of the two steps, i.e., the fast step can be regarded as the change in the Donnan potential on the external solution side (U^{I}), and the subsequent slow step, as the generation of the diffusion potential within the membrane (U_d). The Donnan potential on the internal solution side (U^{II}) remains unchanged during the transition. In this figure, the logarithmic plot of $\{U_m(\infty)-U_m(t)\}$ versus time is also shown, where $U_m(\infty)$ denotes the membrane potential at another steady state after the pH jump. Thus, in the present membrane systems, U_d is thought to change in response to a pH change with a time delay. The whole relaxation curve from the initial steady potential to another steady potential can be divided in two portions to obtain U_d and U_b ($=U^{I} - U^{II}$), assuming that U^{I} remains unchanged during the generation of U_d. Because the ionic flow in the membrane interior is considered to be much slower than that at the interface, this condition should be held. The results are shown in Figure 2.

The condition of the Donnan equilibrium is expressed as

$$y_i^{(\alpha)} c_i^{(\alpha)} = a_i^{\alpha} b_i \exp(-FU^{\alpha}/RT) \qquad \alpha ; \mathrm{I, II}: \ i ; \mathrm{Na, H} \qquad (1)$$

where y, c, a , and b denote the activity coefficient, the concentration, the activity and the partition coefficient between the membrane and the solution, respectively. F is the Faraday constant, R, the gas constant, and T, the absolute temperature.

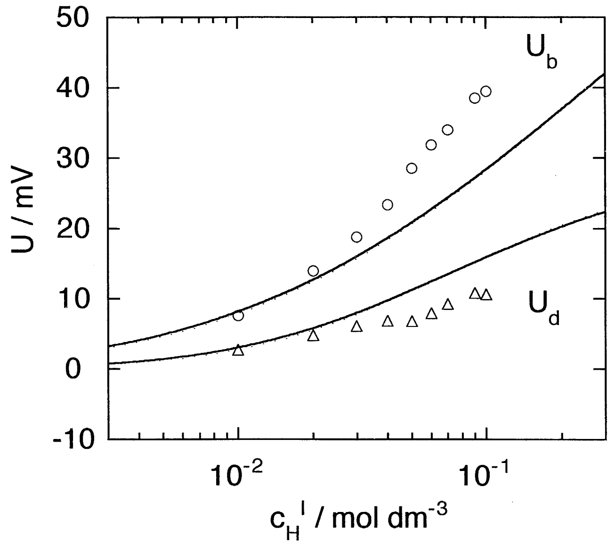

Figure 2. Donnan potential difference, U_b (○), and Diffusion potential within the membrane, U_d (△), obtained from the time course of the membrane potential as a function of the concentration of H^+ ions in the external solution. The solid lines indicate the theoretical values.

Subscripts Na and H refer to Na^+ ion and H^+ ion, respectively. Superscripts (I) and (II) refer to the surface in the membrane phase on the external solution side and that on the internal solution side, respectively, I and II, to the external and internal solution, respectively. The co-ions are assumed to be perfectly excluded from the membrane. Taking account of the acid dissociation constant of COOH group of the membrane, K_a, the Donnan potentials, U^I and U^{II} are given by[6]

$$\exp(-FU^{\alpha}/RT) = \frac{-B_{\alpha} + (B_{\alpha}^2 + 4B_{\alpha}A_{\alpha}c_S^T)^{1/2}}{2B_{\alpha}A_{\alpha}} \qquad \alpha\ ;\ \mathrm{I, II} \qquad (2)$$

where

$$A_{\alpha} = y_S^{(\alpha)} a_H^{\alpha} b_H / K_a, \text{ and } B_{\alpha} = a_{Na}^{\alpha} b_{Na} / y_{Na}^{(\alpha)} + a_H^{\alpha} b_H / y_H^{(\alpha)}.$$

The subscript S refers to the ion exchange site. c_S^T denotes the total concentration of dissociated and undissociated forms of the ion exchange sites. The intramembrane diffusion potential is expressed in terms of the mobility of ion, u_i, and $c_i^{(\alpha)}$ as[6]

$$U_d = -\frac{RT}{F}\ln\frac{u_{Na}c_{Na}^{(II)} + u_H c_H^{(II)}}{u_{Na}c_{Na}^{(I)} + u_H c_H^{(I)}} \qquad (3)$$

The theoretical values of U_b and U_d in Figure 2 were calculated by using Eqs. 2 and 3, respectively. The values of K_a and u_{Na}/u_H obtained from the best fit of the theoretical curves with the experimental results in the range of low hydrogen ion concentration were 0.21 (mol dm^{-3}) and 0.080, respectively. The activity coefficients of ions in aqueous phases were calculated according to the Debye-Hückel equation. We assumed $y_H^{(\alpha)} b_{Na} / y_{Na}^{(\alpha)} b_H$ and $y_H^{(\alpha)} y_S^{(\alpha)}$ to both be unity. The activity coefficient of each species in the membrane was assumed to be independent of the hydrogen ion concentration, e.g., $y_i^{(I)} = y_i^{(II)}$

Figure 3 shows the ion concentrations at the membrane surface obtained for Na^+ and H^+ ions. The experimental values plotted in this figure were obtained from the experimental values of U_b using Eq. 1. The theoretical curve for $c_i^{(I)}$ was obtained from the theoretical values of Donnan potentials. The ion exchange sites are completely occupied by Na^+ ions at the membrane surface on the internal alkaline solution side so that $c_{Na}^{(II)}$ is approximately equal to c_S^T, which is expressed by the ion exchange capacity, *IEC*, and the specific membrane volume, V_m, as $c_S^T = IEC/V_m$.[6] By using $c_{Na}^{(II)}$ (=2.1 mol dm^{-3}) obtained accordingly, we have calculated $c_i^{(I)}$ from U_b. At a pH region near the apparent pK_a, the state of the membrane would drastically change, e.g., a change in the ion-cluster size. It is thought that this transition has come out as a break in the plot of $c_i^{(I)}$ versus external hydrogen ion concentration. As seen from both Figures 2 and 3, at this concentration region, the experimental values begin to deviate from the theoretical curve calculated by using the parameter fitted to the experimental values in the lower concentration range.

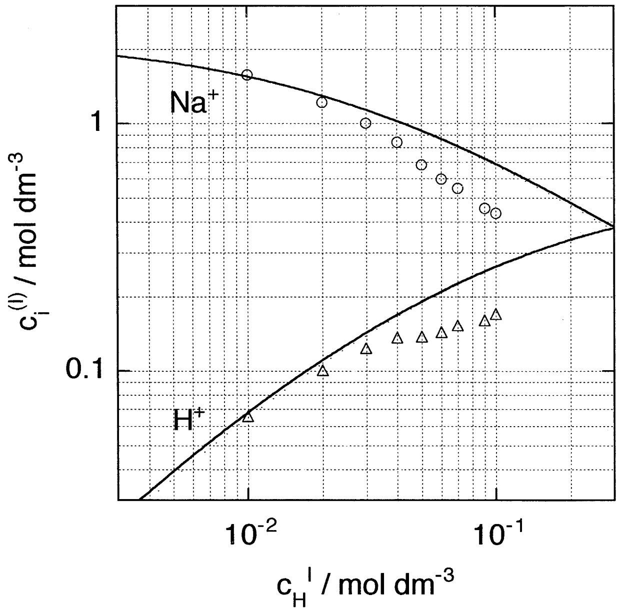

Figure 3. Ion concentration at the surface in the membrane phase on the solution I side as a function of the concentration of H^+ ions in the external solution; ○, $c_{Na}^{(I)}$; △, $c_H^{(I)}$. The solid lines indicate the theoretical values.

References and Notes

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